

Reactive Ion-Surface Collisions: Application of Ionized Acetone- d_6 , DMSO- d_6 and Pyridine- d_5 as Probes for the Characterization of Self-assembled Monolayer Films on Gold

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Low-energy collisions of ionized acetone- d_6 , DMSO- d_6 and pyridine- d_5 with alkanethiolate self-assembled monolayer (SAM) surfaces prepared on gold were investigated. These experiments can be used to monitor routinely the condition of the surfaces and to determine whether a surface is acceptable for a given application. In addition to the surface-induced dissociation of the molecular ions, intense peaks corresponding to the addition of H (or D) to the ionized molecules are observed in the ion-surface collision spectra. The relative abundance of the $[M + H(D)]^+$ reaction products was found to be dependent on several variables, including (i) the chemical composition of the monolayers (alkanethiolate, perdeuteroalkanethiolate, fluorinated alkanethiolate), (ii) the chain length of the alkanethiolate monolayers, (iii) the time for which the vapor-deposited Au surfaces are exposed to the thiol solution during surface preparation and (iv) the degree of deliberate damage of the SAM film (70 eV Ar^{++} beam bombardment). The variation in $[M + H(D)]^+$ abundance with induced surface changes illustrates the utility of these adduct ions for the characterization of the quality of the monolayers. The general trend observed is an increase in the $[M + H]^+$ peak with the increased presence of hydrocarbon adsorbates, which in turn is believed to be directly related to increased disorder (inherent or induced) of the monolayer film. The increase in $[M + H]^+$ is seen with a decrease in chain length, with shorter monolayer preparation times, and with an increase in surface damage. In general, a fluorinated surface that has been intentionally damaged by an Ar^{++} beam retains its high-energy deposition characteristics and is appropriate for use as a collision target for many types of projectiles.

INTRODUCTION

A wide range of successful applications of the ion activation technique surface-induced dissociation (SID) has been reported recently.¹⁻²² In these tandem mass spectrometric experiments, projectile ions selected by the first mass spectrometer collide with the surface, and the products are analyzed by the second mass spectrometer. The product ions can be formed by several competitive processes.¹ Surface-induced dissociation involves conversion of a portion of the translational energy of the projectile ion into internal energy, followed by fragmentation of the impinging ion. Charge exchange can result in neutralization of the impinging ion, with a decrease in total ion abundance, i.e. a decrease in the efficiency of SID. Charge exchange may also result in the ionization and subsequent dissociation of material native to the surface (chemical sputtering). Chemical reactions between the projectile and the surface may also occur, resulting in $[M + R]^+$ (R denotes atoms or groups from the surface, e.g. H, D, F,

CH_3). The extent to which an ion undergoes each of these processes depends on the impinging ion, the surface and the collision energy. In general, SID fragment peaks represent the dominant contribution to the spectrum, i.e. the total scattered ion signal consists mainly of the projectile ion and its fragments.

Recently, ordered organic monolayer surfaces²³⁻²⁶ have been used as effective targets for low-energy ion-surface collision experiments.^{1,3-7,9-13} The surfaces consist of alkanethiols chemisorbed on gold to produce a crystalline-like assembly. The monolayers have been well characterized by other techniques²³⁻²⁶ and provide a means of altering the chemical composition of surfaces. The different surfaces can then be used to gain information on the efficiency of SID, the reactivity of different surface-probe combinations and energy deposition into the projectile ions and the monolayer surfaces. In short, a number of self-assembled monolayers with different chemical compositions can be used as models to establish those surface characteristics that lead to desired surface behavior (e.g. enhanced dissociation or reaction).

Although results based on systematic studies of ion-surface collisions with self-assembled monolayers have been reported by Cooks and co-workers^{1,3-7} and Wysocki and co-workers,⁹⁻¹³ these investigations are

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far from complete. Several general conclusions have been reached to date: (i) the alkanethiolate surfaces, and, in particular, the fluorinated surface, have been shown to result in less neutralization in comparison with metal surfaces; (ii) fluorinated alkanethiolate surfaces provide the highest transfer of kinetic energy to internal energy, i.e. the most extensive fragmentation, of projectile ions;^{4,11,13} (iii) for pyrazine³ and benzene,^{4,11} deuterium labeling confirmed that the source of H(D) and CH₃(CD₃) additions is predominantly the monolayer and not the physisorbed material; (iv) for benzene, the relative amount of H addition and the ratio of the CH₃/C₂H₅ additions depend on the chain length of the alkanethiolates;¹¹ (v) polarizable atomic projectiles, such as Cl⁺, Cl⁻, I⁺ and Xe⁺, form unusual adduct ions by reaction with a fluorinated surface;⁶ and (vi) total ion signals measured at the detector and currents measured at the surface can be used to characterize the relative degree of projectile neutralization, and these data correlate with the electron barrier properties of monolayers films observed in solution electrochemistry experiments.¹¹

Together, the above results have improved both our fundamental knowledge and the practical application of the SID activation technique. In order to understand better and ultimately control the parameters associated with SID as an activation technique, further systematic studies are necessary to identify subtle differences between surfaces, to monitor changes in surface condition as a function of different experimental variables and to establish relationships between this information and surface characterization performed by other techniques.²³⁻²⁶

As a continuation of our work on the benzene molecular ion,¹¹ an attempt was made to find a series of reactive projectile ions with which to probe the organic monolayer surfaces. Our hypothesis is that ions of increasing sensitivity to H addition should allow the detection of trace contaminants by increasing the relative abundance of the ion-surface reaction products in the spectra. Ions selected as potential probes of surface quality are acetone, dimethyl sulfoxide (DMSO) and pyridine. Pyridine is a reasonable choice because it is known to produce a dominant [M + H]⁺ ion if hydrocarbon sources are available at the surface.^{2,20,21} A survey of a number of different compounds revealed that the simple acetone and DMSO molecular ions form significant [M + H]⁺ reaction products, and dissociate by a limited number of fragmentation pathways. These ions are also practical choices for routine surface probes because deuterated analogues are available commercially at modest cost.

RESULTS AND DISCUSSION

We present here spectra that result when ionized acetone-*d*₆, DMSO-*d*₆ and pyridine-*d*₅ collide with a fluorinated surface (CF₃(CF₂)₇CH₂CH₂SAu), *n*-alkanethiolate surfaces (C_{*n*}H_{2*n*+1}SAu; C_{*n*} surfaces, *n* = 4, 8, 12, 18), and a perdeuterated surface (C₂₀D₄₁SAu). In addition to the discussion of differences in reactivity for the different projectiles, results are

presented that illustrate the influence of four variables that also affect the ion-surface collision spectra: (i) the chemical composition of the monolayer, (ii) the chain length of the alkanethiolates, (iii) the time for which the gold surfaces are exposed to the thiol solution during preparation of the monolayer and (iv) deliberate damage of the monolayer films with a 70 eV Ar⁺⁺ beam. The use of the perdeuterated surface allows us to monitor the relative concentrations of reactive H(D) from the monolayer chain and from adsorbed materials.

Relative reactivity of the projectiles with the monolayer surfaces

Addition of H(D) to the molecular ions. Previously, experiments showed that the alkanethiolate monolayer is the dominant source of the H(D) and CH₃(CD₃) added to pyrazine³ and benzene^{4,11} molecular ions. Other sources of H(D) could be adsorbed analyte or other physisorbed contaminants, e.g. from pump oil, and the reactivity of the projectile probes with these materials is key to the surface characterization described below.

When each of the selected probes collides with the perdeuterated alkanethiolate surface (Fig. 1), abundant ions corresponding to D addition and fragments of the [M + D]⁺ adduct are detectable (acetone-*d*₆: *m/z* 66 [M + D]⁺; *m/z* 34 [D₂C=OD]⁺; DMSO-*d*₆: *m/z* 86 [M + D]⁺, *m/z* 68 [M + D - CD₃]⁺; pyridine-*d*₅: *m/z* 86 [M + D]⁺, *m/z* 58 [M + D - DCN]⁺). Other ions correspond to the well known fragments of acetone,^{27,28} DMSO²⁹ and pyridine.^{30,31} In addition to the spectra in Fig. 1, data for collisions of unlabeled projectiles with labeled surfaces and labeled projectiles with unlabeled surfaces were acquired, and were used to help confirm the molecular formulae of ions that correspond to adduct ions and their fragments.

The results show that the projectile ions used in this study definitely react with the H or D from the alkyl chains of the monolayer surface. However, when the perdeuterated surface and deuterated projectiles are used, peaks corresponding to H addition are also present [Fig. 1(a)-(c)], although with significantly lower intensity than peaks corresponding to D addition. When labeled surfaces and projectiles are used to acquire the spectra, contamination of the self-assembled monolayers by H-containing analyte material is avoided. This suggests that the source of the minor peak corresponding to added H in Fig. 1 is hydrocarbon-containing pump oils. After a 12 h purge of the instrument with neutral Ar, the low-intensity [M + H]⁺ peaks decreased further, but were never completely removed. Another possible source of hydrogen in the instrument is water. When water was deliberately introduced to the chamber at 10⁻⁷-10⁻⁵ Torr (1 Torr = 133.3 Pa), however no measurable increase in the hydrogen addition was observed. At higher pressures, a decrease in the [M + H]⁺ is observed, possibly owing to a competitive process where the water displaces or covers the hydrocarbon.

When unlabeled alkanethiolate surfaces are used, it is not possible to distinguish between H donation from the alkanethiolate chain versus H donation from trace contaminants [Fig. 2(a)]. Based on the dominant D

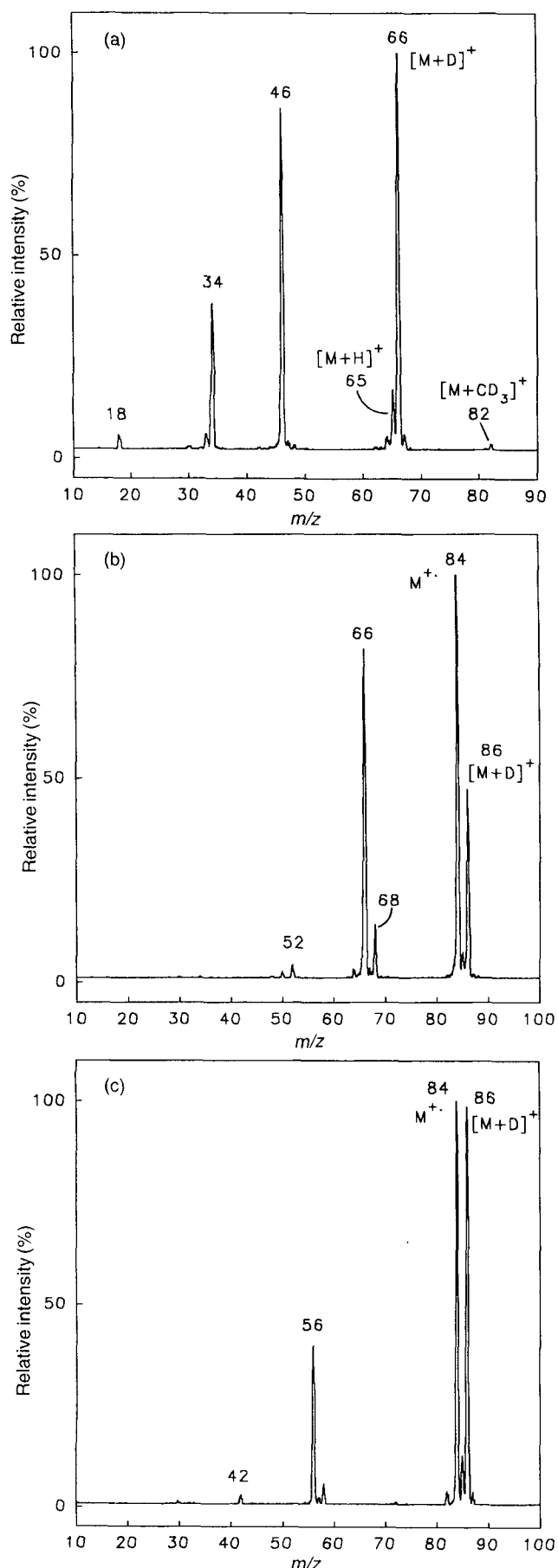


Figure 1. Ion-surface collision spectra obtained by colliding the molecular ions of (a) acetone- d_6 , (b) DMSO- d_6 and (c) pyridine- d_6 at 20 eV collision energy with $C_{20}D_{41}SAu$.

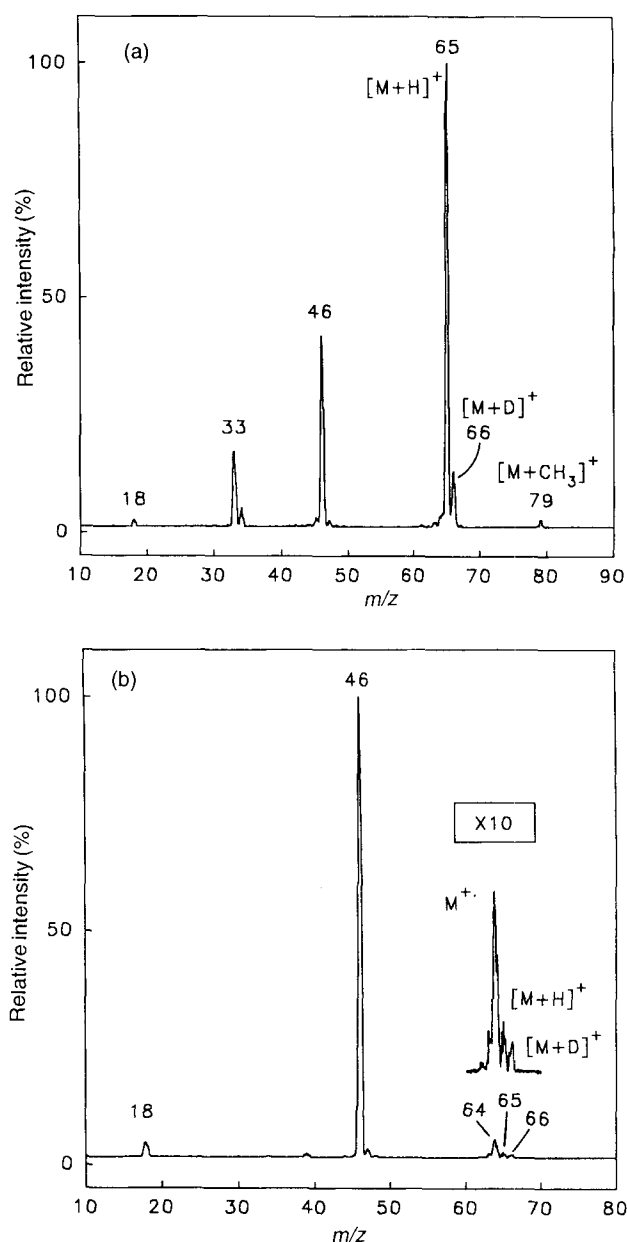


Figure 2. Ion-surface collision spectra obtained by colliding acetone- d_6 molecular ion at (a) 20 eV collision energy with the C_{18} surface and (b) 10 eV collision energy with the fluorinated surface.

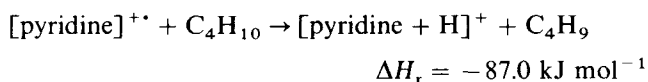
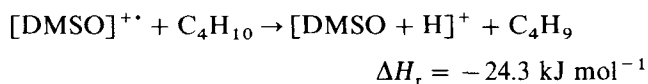
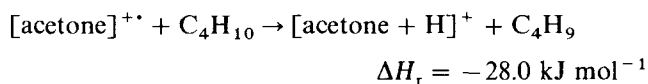
addition from the perdeutero surface, it is reasonable to assume that, if other factors are the same (pressure, collision energy, surface position), the main reaction partner is the monolayer surface and not the physisorbed material. It is important to note that the results in Figs 1 and 2(a) were obtained with films containing long alkanethiolate chains, and that the relative monolayer order²³⁻²⁶ and the relative $[M+H]^+$ contribution (from hydrocarbon contaminants) decrease with increasing chain length (see the next main subsection). The perdeuterated C_{20} monolayer is therefore presented here as an ideal model for a long-chain (unlabeled) alkanethiolate monolayer, with a minimum amount of contamination.

For acetone- d_6 colliding with $CH_3(CH_2)_{17}SAu$ [Fig. 2(a)], a low-intensity peak related to D addition

$[M + D]^+$ is present in the spectrum in addition to the $[M + H]^+$ peak. The appearance of this peak indicates that the acetone- d_6 , and/or its fragments, are also physisorbed on to the alkanethiolate monolayer and can also serve as a partner in the D addition reaction. (The significantly less intense $[M + D]^+$ peaks suggest that the contribution of physisorbed perdeuterated projectile, as a reaction partner, can be neglected for the $[M + D]^+$ formation. Note that $[M + H]^+$ ions formed by chemical ionization in the source were also selected and collided with the surface to determine the main fragmentation products of the adducts.) The physisorbed acetone is presumed to be from the neutral gas, as the D addition is greatly pressure dependent and not seen to any great extent at low pressure, even after continued SID. The $[M + D]^+$ adduct is also detected in the ion-surface collision spectra of acetone- d_6 obtained with the fluorinated surface [Fig. 2(b)]. The adsorption of acetone- d_6 increases with increasing sample pressure and is observed for all surfaces investigated.

Figure 2(b) shows an $[M + H]^+$ peak, in addition to the $[M + D]^+$ peak that originates from adsorption of acetone- d_6 on the fluorinated surface. Formation of the $[M + H]^+$ adduct clearly indicates the presence of physisorbed H-containing material on the fluorinated surface. Pyridine- d_5 also shows trace H-containing adsorbates on the fluorinated surface, with a similar sensitivity to that observed with acetone- d_6 . For DMSO- d_6 , the $[M + H]^+$ peak is of extremely low intensity (see that last main subsection).

The reactivity of the three probes toward H addition from contaminants is in line with the reactivity of the probes toward D addition from the perdeutero monolayer. This is evident from Fig. 1, which shows that the contribution of the reaction products (adducts plus their fragments) to the overall spectrum increases in the order DMSO- d_6 (24%) < pyridine- d_5 (42%) < acetone- d_6 (57%). This order is seemingly inconsistent with the reaction enthalpies calculated for the following model reactions (heats of formation used in these calculations were taken from Ref. 32):



The reaction enthalpies suggest that the pyridine- d_5 molecular ion should be a more reactive projectile than acetone- d_6 and that DMSO- d_6 should have about the same reactivity as acetone- d_6 . Two reasonable explanations for the above discrepancy can be given: (i) the mechanism of H addition is not a simple H transfer from $\text{C}_n\text{H}_{2n+1}\text{SAu}$, negating the validity of the above argument, or (ii) some of the acetone- d_6 molecular ions are excited to the first electronic excited state during the ion-surface collision (above the ground state by about 2.5–3.0 eV³³), analogous to the CID results of Futrell and co-workers²⁷ and Martinez and Ganguli.²⁸ The excited-state acetone molecular ion could be more reac-

tive because of the greater enthalpy change and also the change in the electronic structure. Note that all of the above reactions are predicted to be exothermic, in contrast to reaction with the benzene molecular ion, for which the above reaction is endothermic (+79 kJ mol⁻¹). Recall that the molecular ion of benzene is also a less reactive probe for the detection of trace H-containing contaminants on the fluorinated surface.¹¹

Addition of $\text{CH}_3(\text{CD}_3)$ and $\text{C}_2\text{H}_5(\text{C}_2\text{D}_5)$ alkyl groups. In Figs 1(a) and 2(a), peaks corresponding to $[\text{acetone-}d_6 + \text{CD}_3]^+$ (m/z 82) and $[\text{acetone-}d_6 + \text{CH}_3]^+$ (m/z 79) adduct ions, respectively, are also seen although they are of much lower intensity than the $[M + (\text{H})\text{D}]^+$ peaks. Methyl adducts are also detected for DMSO- d_6 and pyridine- d_5 molecular ions in the collision energy range of 10–20 eV. The appearance of these peaks in the ion-surface collision spectra is common, and has been reported, e.g. for pyrazine³ and benzene.^{2,11} It is of interest, however, that the methyl adducts of acetone and DMSO do not exhibit further loss of H(D) or $\text{H}_2(\text{D}_2)$ at the low collision energies investigated (10–20 eV). Note that for benzene^{2,11} it is the $[M + \text{CH}_3 - \text{H}_2]^+$ fragment (m/z 91) that is dominant.

C_2H_5 and C_2D_5 adducts were detectable only for pyridine- d_5 but with significantly lower abundances than those of the CH_3 and CD_3 adducts. The relative intensity of the peaks corresponding to ethyl and methyl addition is less than 1% of the total ion signal at 20 eV collision energy. The ethyl adducts undergo further fragmentation by the loss of $\text{H}_2(\text{D}_2)$; for example, the $[M + \text{C}_2\text{D}_5]^+ / [M + \text{C}_2\text{D}_5 - \text{D}_2]^+$ ratio (m/z 118:114) is about 1:1 in the 20 eV spectrum obtained with the perdeutero surface.

F addition. Peaks corresponding to F addition ($[M + 19]^+$) were detected for DMSO- d_6 (m/z 103) and pyridine- d_5 (m/z 103). In the case of acetone- d_5 , we could not detect the $[M + \text{F}]^+$ ion unambiguously. The $[\text{DMSO-}d_6 + \text{F}]^+$ ion is not accompanied by peaks corresponding to $[\text{DMSO-}d_6 + \text{F} - \text{D}]$ or $[\text{DMSO-}d_6 + \text{F} - \text{D}_2]$ at 20 eV collision energy, but the relative ratios of the $[\text{pyridine-}d_5 + \text{F}]^+ : [\text{pyridine-}d_5 + \text{F} - \text{D}]^{++} : [\text{pyridine-}d_5 + \text{F} - \text{D}_2]^+$ peaks are 2:1:4. It is interesting that a peak at m/z 104 is also observed in the pyridine- d_5 spectrum and could be $[M + \text{F} + \text{H}]^+$. (Another possible origin of the $[\text{pyridine-}d_5 + \text{HF}]^{++}$ ions could be other adduct ions with higher masses. However, we could not detect any ions in the range m/z 105–120.)

The ability to detect trace hydrocarbon contaminants on the monolayer films provides a tool with which surface characteristics can be monitored. For different instruments, the amounts of background hydrocarbon will, of course, be different as a result of varying pumping mechanisms, base pressures, etc. The degree of $[M + H]^+$ observed and the magnitude of the changes observed here may therefore be different. The relative changes observed as a result of the surface modifications mentioned here are believed to be largely independent of instrumentation. The following sections illustrate several cases where changes in the behavior of the monolayers are prompted and then detected with the probes described above.

Effects of chain length of alkanethiolate surfaces of H addition

It has been shown for benzene molecular ion that H addition and the relative ratio of the $\text{CH}_3/\text{C}_2\text{H}_5$ additions are sensitive to the chain length of alkanethiolate surfaces.¹¹ H addition is less favored and the $\text{CH}_3/\text{C}_2\text{H}_5$ ratio is greater for highly ordered, longer chain alkanethiolates ($\text{C}_n\text{H}_{2n+1}\text{SAu}$; $n = 18, 12$) than for less ordered, shorter chain alkanethiolates ($n = 8, 4$). To investigate whether the same trend is observable for other projectile ions, we carried out a similar study by using acetone- d_6 , DMSO- d_6 and pyridine- d_5 .

The DMSO- d_6 molecular ion represents the best of the three probes for the characterization of the chain length effect for normal unlabeled alkanethiolate monolayer films. Figure 3(a) and (b) show the ion-surface collision spectra obtained by a 20 eV collision of DMSO- d_6 molecular ion with a shorter C_4 surface and

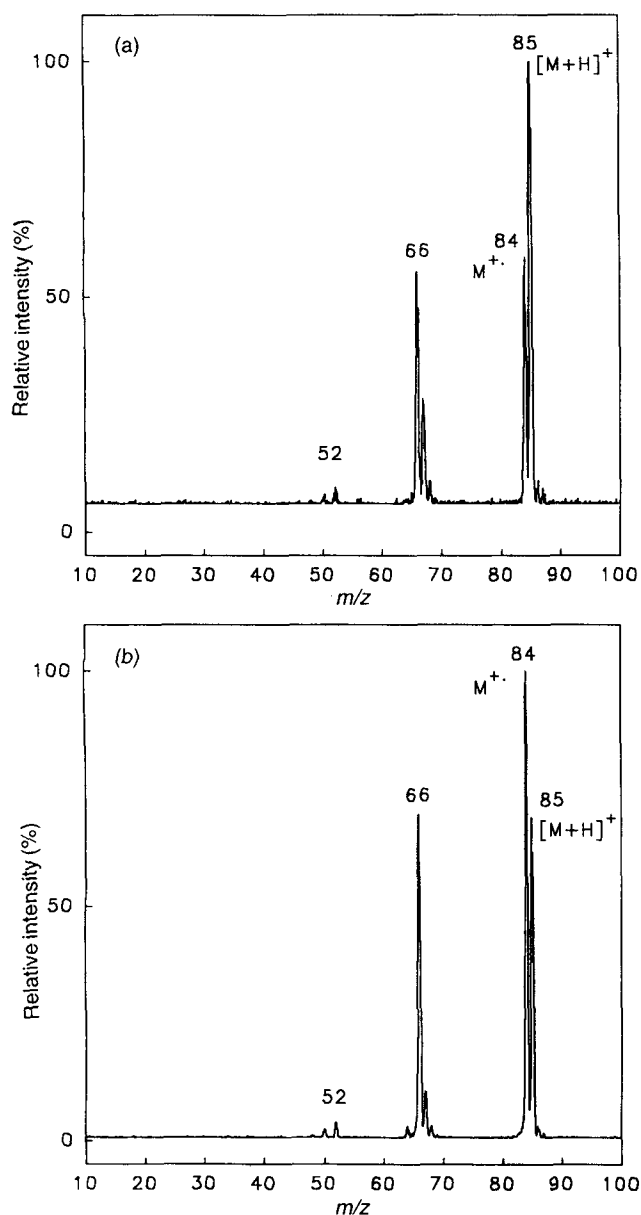


Figure 3. Ion-surface collision spectra obtained by colliding DMSO- d_6 molecular ion at 20 eV collision energy with the (a) C_4 surface and (b) C_{18} surface.

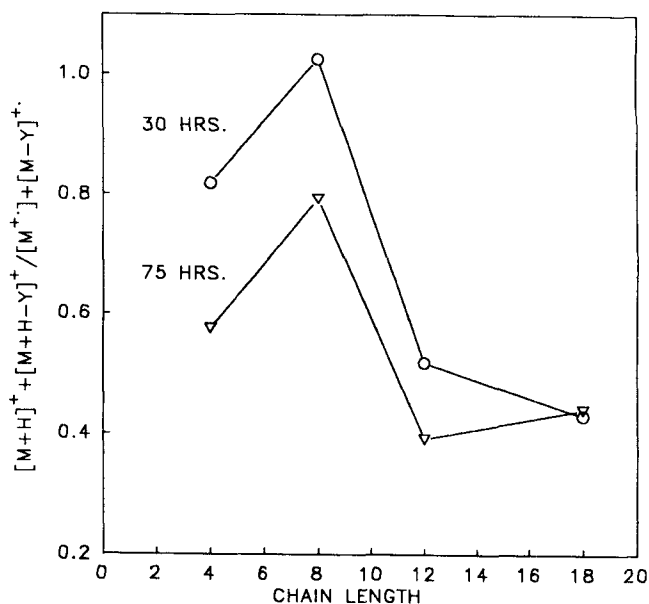


Figure 4. Plot of the $([\text{M}+\text{H}]^+ + [\text{M}+\text{H}-\text{Y}]^+) / ([\text{M}^+] + [\text{M}-\text{Y}]^+)$ ratio, as determined from 20 eV SID spectra of DMSO- d_6 on the alkanethiolate (C_4 , C_8 , C_{12} and C_{18}) surfaces (Y denotes species lost from both $[\text{M}+\text{H}]^+$ and M^+ ; e.g. CD_3). The two lines represent two thiol solution exposure times of 30 and 75 h.

with a longer C_{18} surface, respectively. Figure 4 illustrates the relative abundance ratios of the $[\text{M}+\text{H}]^+$ adduct and resulting fragment ions $[\text{M}+\text{H}-\text{Y}]^+$ versus the molecular ion M^+ and its fragments $[\text{M}-\text{Y}]^+$. It is clear that the $([\text{M}+\text{H}]^+ + [\text{M}+\text{H}-\text{Y}]^+) / (\text{M}^+ + [\text{M}-\text{Y}]^+)$ ratio (i.e. $(m/z\ 85 + m/z\ 67) / (m/z\ 84 + m/z\ 66 + m/z\ 52)$) is greater for the shorter chain C_4 and C_8 surfaces than for the longer chain C_{12} and C_{18} surfaces. This ratio can thus serve as a measure of surface quality. These results and the trends for the above ratio confirm the observations for benzene molecular ion;¹¹ the shorter chain, less ordered C_4 surface results in enhanced H addition reaction. One should remember that the reaction partner is not only the monolayer alkanethiolate but also physisorbed H-containing material (see above). The relative amount of the physisorbed contaminant(s) can be higher on less ordered, shorter chain alkanethiolate monolayers than highly ordered, longer chain monolayers. In contrast to DMSO- d_6 , the molecular ion of acetone- d_6 can be described as too reactive or too sensitive towards the presence of any hydrogen. Nearly all of the undissociated molecular ion signal appears as $[\text{M}+\text{H}]^+$, with the M^+ relative abundance being less than 3% on both the short- and long-chain alkanethiolates. The $[\text{M}+\text{H}]^+ / [\text{M}^+]$ ratio for acetone therefore does not vary significantly with surface composition. Pyridine represents a probe with reactivity intermediate between those of DMSO and acetone.

Effect of preparation time on the monolayers

The plots in Fig. 4 indicate that the solution exposure time of the gold surfaces during preparation of the monolayers also has an effect on the H addition reaction. Although the monolayers are known to be formed within a very short period of time (within seconds),³⁴

the plots in Fig. 4 show that alkanethiolate surfaces prepared for a longer time (75 h) lead to a less intense H addition peak in comparison with monolayer surfaces prepared for a shorter period (30 h). It is also of interest that shorter chain alkanethiolates display a greater sensitivity to the preparation time. Based on these results, we suggest that a second reordering is occurring within the monolayers, as suggested by other investigators of self-assembled monolayers.^{34,35} This effect may have a relationship with the degree of crystallinity or general order of the monolayer films, with longer times in solution resulting in an increase in order, which is clearly detectable by these probes. Further studies are in progress to reveal the fine details of this effect of the chain length and preparation conditions. Knowledge of this increase in order with longer preparation times is of interest because many who use these monolayer surfaces use preparation times of 24 h or less.²³⁻²⁶

Investigation of the durability of the fluorinated monolayer for SID studies.

As was demonstrated above, the H(D)-adduct peaks of acetone-*d*₆, DMSO-*d*₆ and pyridine-*d*₆ can be used to detect trace amounts of H(D)-containing materials on the surfaces. It was also shown that these peaks are sensitive to the preparation time of the monolayers, i.e. they can be related to the quality of the monolayers. The quality of the surface also depends on the time for which the surface is used, i.e. bombarded by (different) projectiles, and on the collision energy. Naturally, a major application of these surfaces is to obtain structural information on the incident ion. How long a surface can be used for SID experiments before changes in its properties (efficiency, energy deposition, chemical sputtering, reaction products) are observed is an obvious

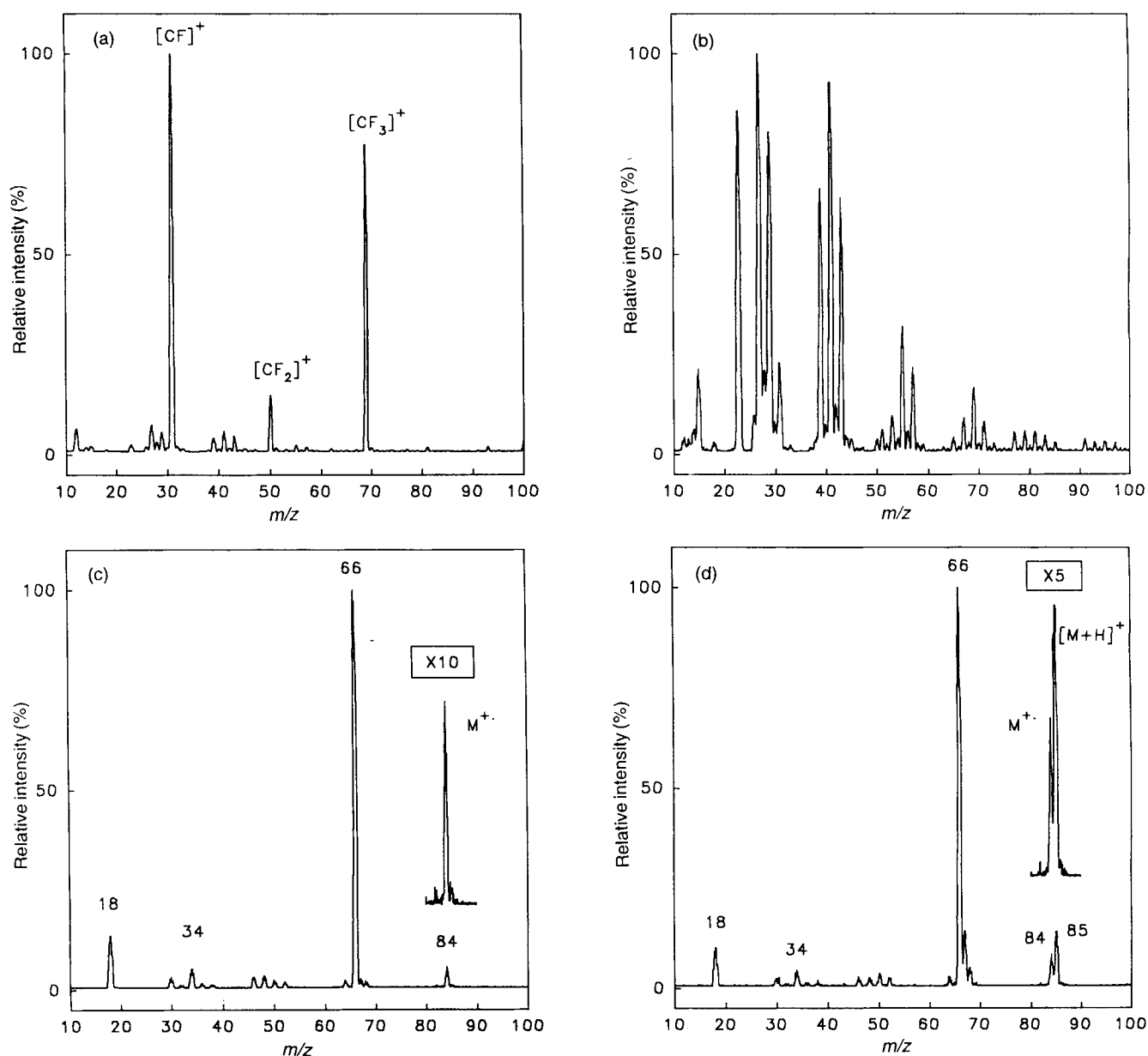


Figure 5. Ion-surface collision spectra obtained by colliding 70 eV Ar²⁺ with the fluorinated surface for (a) 0 h (beginning of bombardment) and (b) 15 h, and the ion-surface collision spectra obtained for the DMSO-*d*₆ molecular ion at 20 eV collision energy with the same fluorinated surface after bombardment with 70 eV Ar²⁺ for (c) 0 h (beginning of bombardment) and (d) 15 h.

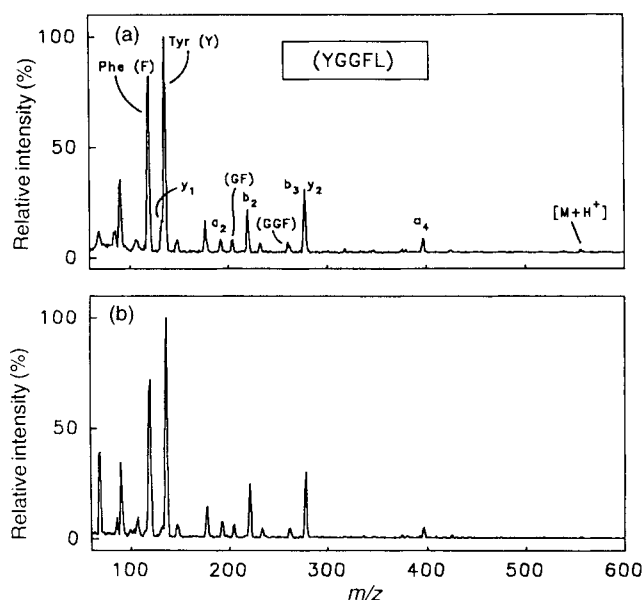


Figure 6. Ion-surface collision spectra obtained by 30 eV collision of protonated leucine enkephalin with the (a) undamaged (0 h) and (b) damaged (15 h) fluorinated surface in Fig. 5.

practical concern. The probes investigated here allow the behavior of a given surface to be monitored during the time it is used as an SID target. It was reported^{6,11,12} that SID spectra are reproducible even after several hours or days of use of the monolayers. This is especially so for large, even-electron ions that do not react with the surfaces.¹² On the other hand, because chemical sputtering becomes enhanced with increasing collision energy, the monolayers can definitely be damaged during the collision, even if the damage is not manifested directly by changes in the fragmentation spectra of the projectile ion. To obtain more information about the damage of the monolayers, we bombarded the fluorinated and deuterated surfaces with higher energy Ar^{++} (70 eV) and checked the surface quality with 20 eV collisions of DMSO-d_6 . Bombardment with Ar^{++} at 70 eV should allow quick damage to the surface because Ar has no vibrational modes to activate and because the high recombination energy of Ar^{++} should lead to significant charge exchange with the surface which is of lower ionization energy.

Figure 5(a) and (b) show the ion-surface collision spectra obtained by 70 eV Ar^{++} bombardment of the fluorinated surface at time zero and after a 15 h bombardment, respectively. These are sputtering spectra, i.e. all ions that are detected (other than Ar^{++}) originate from the surface. This means that the atomic Ar^{++} ion undergoes a charge-exchange process with the surface and the resulting charged surface species has enough excess (vibrational) energy to fragment. It is seen in Fig. 5(a) that at the beginning of the bombardment the dominant ions are all F-containing ions (m/z 31 CF^+ , m/z 50 CF_2^+ , m/z 69 CF_3^+) and peaks corresponding to hydrocarbon fragments are of very low intensity (see, e.g., m/z 43, 41, 29 and 27). However, after a 15 h bombardment [Fig. 5(b)], the hydrocarbon peaks become dominant and the fluorocarbon peaks are of significantly lower intensity. It is interesting that the intense peak at m/z 23 corresponds to Na^+ , the origin of which is presumably the solution used in the preparation of

the 2-(perfluorooctyl)ethanethiol.¹¹ The dominance of hydrocarbon sputtering ions in Fig. 5(b) suggests that, during bombardment, the fragmentation of the fluorocarbon chains leads to active centers on which the H-containing species are easily and extensively adsorbed. The number of these active centers increases with increasing time of bombardment, which leads to increasing amounts of physisorbed hydrocarbon.

Looking at Fig. 5(b), one would think that the damaged surface is far from a 'good-quality' fluorinated surface for SID. Nevertheless, the comparison of the ion-surface collision spectra obtained for DMSO-d_6 on the same fluorinated surface before [Fig. 5(c)] and after [Fig. 5(d)] damage suggests that the damaged surface can still be regarded as a reliable surface, as far as the fragmentation of the molecular ion is concerned. The internal energy deposited to the molecular ion is largely the same, which leads to the abundant $[\text{M} - \text{CD}_3]^+$ fragment (m/z 66) and abundant CD_3^+ cation (m/z 15). Nevertheless, the relative intensity of the $[\text{M} + \text{H}]^+$ peak is significantly higher for the damaged surface, confirming the increased amount of physisorbed hydrocarbon on the fluorinated surface. Note that a similar trend was observed for the perdeuterated surface; the hydrocarbon:deuterocarbon ratio increased with increasing time of bombardment but the fragmentation of the projectile ion was found to be similar. The changes in the relative abundance of $[\text{M} + \text{H}]^+$ for acetone- d_6 and DMSO-d_6 is a more sensitive measure than changes in the SID energy deposition of the surface.

It was also desirable to investigate the effect of surface damage on spectra for a projectile which is known to be unreactive with the surface. We rarely observe reaction products for protonated oligopeptides.¹² Figure 6(a) and (b) show the ion-surface collision spectra of protonated leucine enkephalin obtained on the same fluorinated surface at zero time (undamaged) and after a 15 h bombardment with 70 eV Ar^{++} (damaged), respectively. The relative intensities of the peaks are largely identical and information necessary for sequence analysis is available from both spectra. Note also that the extent of fragmentation is consistent with the higher energy deposition associated with a fluorinated surface. The higher $[\text{M} + \text{H}]^+$ abundance is consistent with contaminant adsorption to active sites, as mentioned above. The practical implications of these results are that the self-assembled monolayer surfaces lead to highly reproducible spectra even under damage conditions (e.g. 70 eV Ar^{++}) that are more severe than normal operating conditions. The relative extent of projectile neutralization, however, increases with surface damage and requires further investigation.

CONCLUSION

Probes able to assess surface quality are of great importance when attempting to enhance and control ion-surface collision experiments. The molecular ions of perdeuterated acetone, DMSO and pyridine represent sensitive projectiles with which to characterize self-assembled monolayer films. Each probe exhibits a dif-

ferent degree of sensitivity towards the reaction with available hydrogen (or deuterium) and the intensity of the $[M + H(D)]^+$ adduct reflects the relative order and quality of the monolayers. In confirmation with the results obtained for benzene,¹¹ the shorter chain C_4 and C_8 alkanethiolate surfaces behaved differently from the longer chain C_{12} and C_{18} surfaces. The relative H addition also depends on the preparation time of the monolayers. The longer (75 h) preparation time presumably provides more ordered monolayers, because under these conditions the characteristics of the short-chain materials approach those observed for long chains. Qualities associated with 'good' and 'useful' surfaces for SID in our laboratory are generally those which do not render abundant $[M + H]^+$ reaction products in the spectra of perdeuterated acetone, DMSO and pyridine. Of these three, pyridine is perhaps the most limited in practical utility, as it is damaging to instrument components containing Viton O-rings, septa or sleeves. The relative intensity of the $[M + H]^+$ peaks increases with increasing time of surface bombardment (by a damaging projectile such as Ar^{++}), indicating the damage of the monolayers and the increasing amount of physisorbed contaminant on the surface. Nevertheless, the fragmentation patterns of non-reactive projectile ions are not affected significantly.

For routine and regular tests, we recommend the molecular ions of acetone- d_6 and DMSO- d_6 . These probes can be employed to check and monitor surfaces during the course of an experiment and will be used in the near future for testing not only self-assembled monolayers but also other types of surfaces.

EXPERIMENTAL

The tandem mass spectrometer used in this investigation has been described²² and has been applied recently for several surface-induced dissociation studies.⁸⁻¹³ The instrument consists of two Extrel 4000 u quadrupoles positioned at 90° , with a surface placed to intersect the ion optical path of the two quadrupoles. The surface is rotatable in the z-axis (Q1 and Q2 in the x-y plane) and

positioned 45° relative to the surface normal. A probe capable of holding four surfaces inside the instrument at one time was employed to guarantee a similar laboratory environment for the different monolayer types. All projectile ions were produced by 70 eV electron impact ionization, with the exception of protonated leucine enkephalin, which was formed by 6 keV Cs^+ ion bombardment (liquid secondary ion mass spectrometry). With the following exception, the collision energy was kept at 20 eV for the probe ions because at this energy the degree of ion fragmentation is limited. Acetone- d_6 spectra were obtained at 10 eV on the fluorinated surface to further limit fragmentation. Ar^{++} damage experiments were performed at 70 eV and leucine enkephalin spectra were obtained at 30 eV. The pressure in the analyzer region was kept within the range $5.0-5.5 \times 10^{-7}$ Torr for acetone and DMSO and $8 \times 10^{-7}-9 \times 10^{-7}$ Torr for Ar^{++} . Base pressures were routinely $7.5 \times 10^{-8}-2.0 \times 10^{-7}$ Torr. The pressure was measured with a Granville-Phillips nude ion gage, positioned behind the surface holder and inside a metal tube located 5 in (1 in = 2.54 cm) from the surfaces. Unamplified currents were measured at the surface using a Keithley 485 picoammeter and a stainless-steel target, as a crude description of the Ar^{++} flux. Currents of the order of 1-5 nA were measured for pressures of 8×10^{-7} Torr. Unpublished condensed-phase wetting experiments³⁶ carried out in this laboratory³⁷ suggest that the ion beam is 2-3 mm in diameter.

Self-assembled monolayer films were prepared by the spontaneous assembly of (2-perfluorooctyl) ethanethiol ($CF_3(CF_2)_7CH_2CH_2SH$), octadecanethiol ($CH_3(CH_2)_{17}SH$), dodecanethiol ($CH_3(CH_2)_{11}SH$), octanethiol ($CH_3(CH_2)_7SH$), butanethiol ($CH_3(CH_2)_3SH$) and perdeuterioeicosanethiol ($CD_3(CD_2)_{19}SH$) on to vapor-deposited gold. The films were prepared by immersing the gold substrate in 5 mM thiol solution for 30 h. For experiments involving solution exposure times, surfaces were prepared for 30 and 75 h. (For further details on the surface preparation, see Ref. 11.)

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